

THERMODYNAMIC CHARTS FOR THE
COMBUSTION PROCESS IN DIESEL
CYCLES

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P. E. SWIDERSKI

THESIS
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U. S. Naval Postgraduate School
Monterey, California

THERMODYNAMIC CHARTS
FOR THE COMBUSTION PROCESS
IN DIESEL CYCLES

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F. E. Swiderski

THE HISTORY OF THE
CITY OF BOSTON
FROM 1630 TO 1800
BY
J. B. HARRIS

NEW YORK
1880

PREFACE

Though a number of thermodynamic charts for internal combustion processes have been prepared in the past two decades, the project by Lt. William F. Farrell, Jr., USN, "Thermodynamic Chart for The Combustion Process in Diesel Cycles", was one of the first to cover the pressure, temperature and a typical fuel-air ratio of diesel cycles.

This project presents thermodynamic charts of two diesel fuel-air ratios, being assumed maximum and minimum ratios that would be used in diesel cycles, covering the temperatures and pressures used by Lt. Farrell in his project. Thus this is a continuation of the project started by him. The ratios used will enable the user to extrapolate or interpolate between the values used by the author and those of Lt. Farrell.

Of a necessity, much of the written material is a repetition of the work done by Lt. Farrell. Much of Lt. Farrell's work and methods have been checked.

The analysis and computations necessary for this project and the construction of the thermodynamic charts was made during the period February, 1952 through June, 1952, by the author.

[illegible]

THERMODYNAMIC CHARTS
FOR THE COMBUSTION PROCESS
IN DIESEL CYCLES

by

Francis E. Swiderski
Commander, United States Navy

Submitted in partial fulfillment
of the requirements
for
CERTIFICATE OF COMPLETION OF CURRICULUM
in

Mechanical Engineering

United States Naval Postgraduate School
Monterey, California
1952

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Table I

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LIST OF SYMBOLS

| | |
|-----------------|--|
| P | Pressure (total), in atmospheres |
| P_i | Pressure (partial), in atmospheres |
| p | Pressure (total), lbs./sq. in. |
| T | Temperature, °Rankine |
| V | Volume, cubic feet |
| E | Internal Energy, B.T.U., above CO_2 , H_2O (vapor), O_2 and air- N_2 at 100°F. |
| E_s | Sensible Internal Energy, $(E - Q_v)$, in B.T.U. |
| Q_v | Internal Energy of Combustion, at 100°F., of unburned fuel in equilibrium mixture at temperature T , in B.T.U. |
| H | Enthalpy, B.T.U., $E + J(pV)$ |
| S | Entropy, B.T.U./°Rankine, above CO_2 , H_2O (vapor), O_2 and air- N_2 , each at one atmosphere and 100°F |
| R | Universal gas constant |
| J | Conversion factor, 1 B.T.U. = 778 ft. lbs. |
| k | Mean Specific Heat Ratio |
| $K_1 - K_c$ | Equilibrium constants |
| \mathcal{X}_i | Mole fraction of each chemical species at equilibrium |
| n | Moles of each chemical species at equilibrium |
| $\sum n$ | Total moles of combustion products |

| | |
|------------------------------|-----|
| Volume (total), in thousands | P |
| Volume (total), in thousands | P |
| Volume (total), in thousands | P |
| Volume (total), in thousands | T |
| Volume (total), in thousands | V |
| Volume (total), in thousands | E |
| Volume (total), in thousands | E |
| Volume (total), in thousands | Q |
| Volume (total), in thousands | H |
| Volume (total), in thousands | S |
| Volume (total), in thousands | R |
| Volume (total), in thousands | J |
| Volume (total), in thousands | K |
| Volume (total), in thousands | K-K |
| Volume (total), in thousands | J |
| Volume (total), in thousands | W |
| Volume (total), in thousands | Z |

CHAPTER I

INTRODUCTION

The large fraction of combustion processes of interest to the engineer involves burning of a hydrocarbon of fairly moderate volatility in air. For purposes of analysis by thermodynamic chart, an internal combustion engine cycle may be divided into (A) low temperature regions where chemical dissociation does not occur, or negligible in importance, and (B) high temperature regions, reached in the combustion of the fuel, where chemical dissociation may become of appreciable magnitude.

Charts prepared by H. C. Hottel, G. C. Williams and C. N. Satterfield in 1949 (2), cover both the above regions for the gasoline engine cycle, and are satisfactory for use with diesel engine cycles in region (A). They do not, however, cover the temperature range and pressure range of the diesel during combustion, i.e., in region (B).

The thermodynamic charts presented in this project cover the pressure and temperature range of the combustion portion of the diesel cycle for two limiting diesel fuel-air ratios. They have been constructed on the same material and temperature bases as charts for gasoline engines in region (B), and thus may be used in conjunction with charts representing the unburned mixture, as prepared by Hottel, Williams and Satterfield (2). Values of equilibrium constants and thermodynamic property values used here are consistent with those used by Hottel, Williams and Satterfield (2).

CHAPTER 1
INTRODUCTION

The first chapter is devoted to a general discussion of the

principles involved in the study of the properties of the

functions of the complex plane. It is shown that the

functions of the complex plane are characterized by the

following properties:

1. The function $f(z)$ is analytic in the domain D if and

only if it satisfies the Cauchy-Riemann conditions in D . The

converse is also true.

The second chapter is devoted to the study of the

properties of the functions of the complex plane. It is shown

that the functions of the complex plane are characterized by the

following properties:

CHAPTER II

BASIC CONSIDERATIONS AND DATA

1. Data Used

It was suggested by Professor D. Kavanaugh, of the Engineering School, of the United States Naval Postgraduate School, that the charts to be constructed have fuel-air ratios below and above the fuel-air ratios used by Lt. Farrell. The following data was used:

Fuel-Air Ratio: 0.77 (130% theoretical air).

0.40 (250% theoretical air).

Pressure Range: 800 p.s.i. to 1500 p.s.i.

Temperature Range: 3000° Rankine to 4500° Rankine.

2. Chemical Dissociation

At the high temperatures reached in the combustion process of the diesel engine there may be many different molecular species present in varying amounts, due to chemical dissociation of the working fluid. The requirement of chemical equilibrium necessitates consideration of the effect of the species on the thermodynamic properties of the burned mixture. There are ten molecular species (N_2 , O_2 , CO_2 , H_2O , NO , OH , CO , O , H_2 , and H) present in sufficient quantity to require consideration in this development. In the course of this project, it was found that the effects of the minor species (NO , OH , CO , O , H_2 , H) were of definite importance in the temperature and pressure range used. In Figure 1. is shown the effect of temperature on the relative magnitude of these species for one representative pressure for both fuel-air ratios. It is apparent that the magnitudes of these minor species become appreciable

Graph showing the specific heat (C_p) versus temperature ($^{\circ}R$) for 100 g. of propene. The y-axis represents C_p (ranging from 1 to 10) and the x-axis represents temperature in $^{\circ}R$ (ranging from 3000 to 4500). The curve shows a sharp increase in C_p around 3500 $^{\circ}R$.

 CO_2 H_2O

NO

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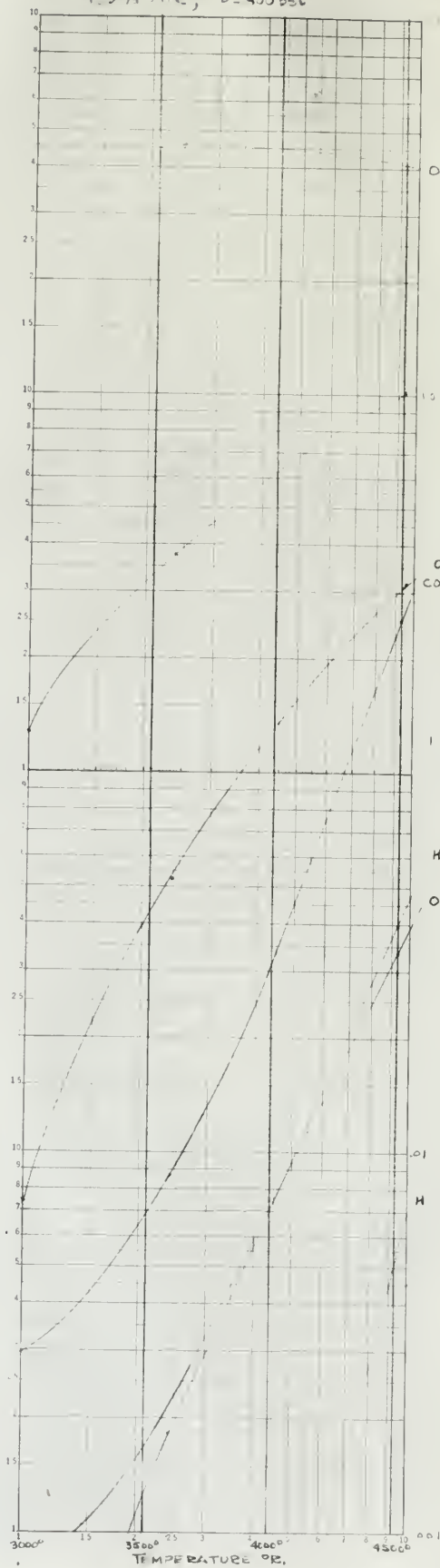
1892

1893

100% Air, D=900 psu

COMPOSITION % BY VOLUME

Fig. 19 EFFECT OF TEMPERATURE ON THE COMPOSITION OF AIR



at the higher temperatures, and cannot be neglected in computations, without resulting error. Particularly is this true of the species NO and OH, which frequently are neglected in determinations of burned mixture composition.

3. Ideal Gas Law

Computations involving composition of the burned mixture together with critical pressures and temperatures of the component species indicate that the burned mixtures behave as if their critical pressures and temperatures are approximately 30 atmospheres and 350° Rankine, respectively. At the elevated temperatures of the chart deviations from the ideal gas law are insignificant. Therefore, the chart is based on the equation of state for ideal gases.

4. Fundamental Data

The fundamental data required for calculation of these charts are: (a) equilibrium constants as functions of temperature, and (b) various heats of reaction. The author has accepted for his calculations the same data on internal energies, enthalpies, entropies, and equilibrium constants as did Hottel, Williams and Satterfield (2), and the computations of Lt. Farrell based on the above. The method of determining the changes in the thermodynamic properties for the chemical reaction in question is given in Appendix I, page 21; the method of obtaining the actual equilibrium constants used in the calculation of composition of combustion products in equilibrium at the various temperatures and pressures is described briefly in Appendix I, page 19.

Composition of air: On a basis of 100 moles of dry air, a composition of 20.99 moles of oxygen and 79.01 moles of nitrogen was used. In

at the light microscope, the amount of material is estimated, and the amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope.

2. Ideal gas law

Deviations involving comparison of the actual behavior of gases with ideal behavior and comparison of the actual behavior of gases with ideal behavior. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope.

3. Fundamental data

The fundamental data are given in the following table. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope.

Comparison of the amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope. The amount of material is estimated at the light microscope.

actuality, the nitrogen above has minor components of argon, carbon dioxide, and hydrogen included, and might better be called Air-Nitrogen. The above composition was used in calculating thermodynamic properties; but pure nitrogen was used in equilibrium calculations, which made but a negligible change in the amount of NO present.

Composition of fuel: The fuel chosen was the hydrocarbon $(CH_2)_x$, which has a hydrogen-carbon ratio considered adequately representative of diesel fuel.

Other constants:

1. Gas Constant $R = 1.987 \text{ cal./}^\circ K, \text{ gram-mole.}$
2. Apparent Formula Mass of Air - 28.95 (which agrees with the above air composition.)
3. Atomic masses from 1936 International Tables.
4. Conversion Factor: 1 atmosphere - 14.696 p.s.i.
5. Conversion Factor: 1 cal./gram-mole - 1.80 BTU/lb.-mole.
6. Conversion Factor: 1 lb.-mole burned mixture - 0.0024135 lb. of air.

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CHAPTER III

PROCEDURE

1. Analysis

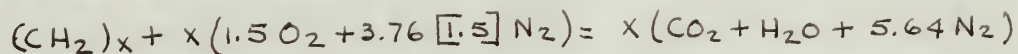
If definitely fixed quantities of carbon, hydrogen, oxygen and nitrogen are permitted to come into equilibrium, two of the properties of the resultant mixture may be fixed, and will be sufficient to completely define the composition of the mixture, and hence its thermodynamic properties. Pressure and temperature were the properties selected in this work.

It was considered that the chemical dissociation would produce combustion products containing the following molecular species: N_2 , O_2 , CO_2 , H_2O , CO , H_2 , H , OH , O and NO . The relative magnitudes of these species, at the fixed fuel-air ratio, depend on the pressure and temperature. The method used to calculate these magnitudes at a sample pressure and temperature, using determined data on equilibrium constants, is shown in Appendix II.

2. Material Basis

The material basis of the chart is the quantity of material which contains nitrogen and oxygen equivalent to one pound of air.

For complete combustion:



For a fuel-air ratio of 0.77, there are 1.95 moles of oxygen and 7.332 moles of nitrogen, or 9.282 moles of air, for each CH_2 unit of fuel. The mass of air is $(9.282)(28.95) \approx 268.714$ pounds; the mass of fuel $(1)(12) + (2)(1.008) \approx 14.016$ pounds. The mass of fuel associated with one pound of air is then 0.05216 pounds. For a fuel-air ratio of 0.40, there are 3.75 moles of oxygen and 14.1 moles of nitrogen, or 17.85 moles of air, for

REPORT III

EXPERIMENT

1. Analysis of the sample.

1.1. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g. The residue was then dissolved in 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

1.2. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g. The residue was then dissolved in 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

1.3. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

1.4. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

1.5. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

1.6. The sample was found to contain 0.10% of water, hydrogen, oxygen and nitrogen and was dissolved in 100 ml. of water. The solution was then treated with 10 ml. of 10% sodium hydroxide solution and the mixture was allowed to stand for 24 hours. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was then weighed and found to be 0.10 g.

each CH_2 unit of fuel. The mass of air is 14.016 pounds. The mass of fuel associated with one pound of air is then .027123 pounds. The mass basis is necessary for consistency because the number of moles of combustion products varies at elevated temperatures with variation of any thermodynamic property.

3. Determination of Thermodynamic Properties

The temperature base for the chart was selected as 100°F . The values of internal energy and entropy, obtained from Table 6, Appendix A, Hottel, Williams, and Satterfield, (2) were converted to this temperature base as described and illustrated in Appendix I. To determine the internal energy of the combustion products at each selected temperature and pressure, the procedure is to multiply the mole fraction of each molecular species in the products, by its corresponding value of internal energy, corrected to proper temperature base, sum up these products for all ten species, and convert to the proper material basis for the chart; thus

$$E_{\text{mix}} = \sum \gamma_i E_i$$

Entropy involves not only an additive factor similar to that shown above for internal energy, but also the entropy of mixing; that is, the entropy of the mixture is

$$S_{\text{mix}} = \sum (\gamma_i S_i - \gamma_i R \ln P_i)$$

where γ_i is the mole fraction of each species, S_i is the molar entropy of each species at one atmosphere pressure and each temperature, corrected to the proper temperature base, R is the gas constant, and P_i is the partial pressure of the components, in atmospheres, and also equals $\gamma_i P$, where P is the total pressure of the mixture in atmospheres. The entropy S_{mix} is corrected to the proper material base for

with life and it shall, The man of his own power. The man of law
associated with the world as well as with the world's people. The man who
is necessary for himself as well as for the world of men.
The man who is at all times engaged with the world of all things.

Gordon Wright

40. *Chlorophyll a* (100%)

The following table shows the results of the analysis of variance for the effect of the type of soil on the yield of the different varieties of wheat.

It is always a good idea to have a backup of your data before making any changes.

Source: *Journal of the American Statistical Association*, 1970, 65(326), 110-111.

minutes of the 1st meeting of the Department of the Interior, 1892-1893.

*All interest rates are subject to change without notice.

10. *Construct a new variable, Y_{it} , which is the logarithm of the variable Y_{it} .*

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$$\mathbb{E} W = \infty$$

Source: *Journal of the American Statistical Association*, 1970, 65, 1, 1-11.

and their control to protect and enhance the common heritage of all people.

U.S. Department of the Interior

$$\sum_{j=1}^n (x_j - \bar{x})^2 = \sum_{j=1}^n x_j^2 - n\bar{x}^2$$

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6. Government does not exercise standards and is believed open to

Approved for the Director of the Department of Defense, 1994

B. = ein weiterer Versuch mit einem anderen Versuchstier

[illegible]

the chart. The enthalpy of the mixture is obtained from the thermodynamic relation

$$H_{mix} = E_{mix} + p \frac{V}{J} = E_{mix} + RT$$

The volume at each pressure and temperature is obtained from the ideal gas law:

$$V_{mix} = (\sum m) R' T / 144 p$$

where $(\sum m)$ is the total moles of the mixture at each temperature and pressure, R' is the gas constant (1545 BTU/°R. lb-mole) and p is the total pressure in pounds per square inch. This volume is then converted to the proper material basis of the chart.

4. Description of Chart

The thermodynamic properties represented on the chart are as follows:

(a) Temperature - T , degrees Rankine. Nearly horizontal solid lines at 200 degrees intervals.

(b) Pressure - p , pounds per square inch. Diagonal solid lines at 100 p.s.i. intervals.

(c) Volume - V , cubic feet per pound of original air. Diagonal dashed lines with greater slope than the pressure lines, at 0.1 or 0.2 cubic foot intervals.

(d) Internal Energy - E , BTU per pound of original air. Ordinate of chart.

(e) Entropy - S , BTU/°Rankine per pound of original air. Abscissa of chart.

(f) Enthalpy - H , BTU per pound of original air. Nearly horizontal dashed lines, superimposed on the chart to eliminate the necessity of using the relation $H = E + RT$.

$$H_{mix} = E_{mix} + \frac{V}{V} = E_{mix} + RT$$

$$V_{mix} = (E_{mix}) / (RT)$$

5. Method of Reading the Chart

To illustrate reading the chart let it be desired to determine the thermodynamic properties of the products of combustion of one pound of air with $(CH_2)_x$ vapor at T 3600° Rankine and p 1200 p.s.i. The original mixture contains 150% excess air. Locate the intersection of the lines corresponding to the above temperature and pressure, and read directly that the volume is 1.8 cubic feet; the internal energy is 682.1 BTU; the enthalpy is 947.2 BTU; and the entropy is 0.269 BTU/° Rankine. Interpolation between temperature and enthalpy lines is substantially linear. In actual cycle analysis employing the chart, the known thermodynamic properties will be more probably pressure and either internal energy or enthalpy, but the procedure in reading the chart remains the same.

6. Use of the Chart.

The chart is designed for use in conjunction with diagrams representative of the unburned mixture existing prior to combustion, in analyzing diesel cycles. Such diagrams have been prepared by Hottel, Williams, and Satterfield, (2). The author's charts indicate the thermodynamic properties of the burned mixture as a result of the combustion process.

[illegible]

1. The first is the fact that the Commission has not yet received any information from the Government of the United States regarding the results of its investigation of the activities of the Communist Party in the United States.

CHAPTER IV

A DISCUSSION OF THE SYSTEM BELOW 3000° RANKINE

1. Basic Requirements.

To permit determination of the thermodynamic properties of the burned mixture as a result of isentropic expansion to a point where the exhaust valve opens, a low pressure-low temperature chart, of substantially the same entropy limits as the author's chart, is required. The approximate temperature and pressure ranges for this chart are 900° Rankine to 2900° Rankine, and 14.7 p.s.i. to 180 p.s.i. respectively.

2. Frozen Equilibria.

Chemical equilibrium has been assumed to exist at all temperatures above 3000° Rankine, where the chemical reaction velocity is quite high. However, when the gas mixture is rapidly cooled below 3000° Rankine, the composition is found to correspond to that at some higher temperature, at which the composition "froze". Considering that in diesel cycles an isentropic path is closest to the actual path to the system below 3000° Rankine, the pressure effect on composition was taken into account by the assumption that the composition of a mixture below 3000° Rankine, was that of the mixture at 3000° Rankine, at the same entropy. Experimental validation of this assumption is quoted in Chapter V, Robinson (5), and is consistent, in this temperature and pressure range, with the value of 2850° Rankine, used by Hottel, Williams, and Satterfield (2).

3. Determination of Thermodynamic Properties.

The composition of the burned mixture at 3000° Rankine and at various pressures is determined as shown in Appendix II. The entropy

A SUMMARY OF THE FACTS CONCERNING THE

1. THE FACTS

The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the...

2. THE FACTS

The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the...

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4. THE FACTS

The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the... The purpose of this chapter is to present a summary of the facts concerning the...

of the mixture at 3000° Rankine and the above pressure is determined as described in paragraph 3 of Chapter III. As stated in paragraph 1 above, the composition of the burned mixture at any temperature below 3000° Rankine is that of the mixture at 3000° Rankine at the same entropy. Thus, selection of any temperature T in this region fixes two thermodynamic properties - temperature and entropy - and these are sufficient to define the remaining thermodynamic properties of the mixture. The internal energy and enthalpy at each temperature T is then obtained in the manner described in paragraph 3, Chapter III, using the mixture composition at 3000° Rankine at each entropy. To obtain pressure (p) and volume (V), the equations for the isentropic process by which this region is entered in the cycle, from the region above 3000° Rankine, are used. These are, at any temperature T and entropy S:

$$p = p_1 \left(\frac{T}{T_1} \right)^{\frac{k}{k-1}} \quad \text{and} \quad V = V_1 \left(\frac{T_1}{T} \right)^{\frac{1}{k-1}}$$

where p_1 and V_1 are the pressure and volume at $T_1 = 3000^\circ$ Rankine, and k is the mean specific heat ratio between the temperature T and T_1 . Values of the specific heat ratio for the $(CH_2)_x$ fuel with 130% and 250% air, at any temperature between 300° Rankine and 4000° Rankine, may be obtained from tables in the Gas Tables (3), by interpolation and extrapolation. The method of obtaining the mean specific heat ratio between any two temperatures, when the specific heat ratios at these limiting temperatures are known, is set forth in Kiefer, Stuart and Kinney (4).

at the above 3000° indicated the same pressure as indicated
 as indicated in paragraph 4 at 3000° 111. It is noted in paragraph 1
 above, the composition of the burned mixture is not indicated. This
 3000° mixture is that of the mixture at 3000° burned at the same
 mixture. This, subject of the mixture is at this point. This
 the thermodynamic properties of the mixture and mixture and these are
 indicated by the thermodynamic properties of the
 mixture. The thermodynamic properties of the mixture are
 given in the same manner as in paragraph 4, Section 111, being
 the mixture composition at 3000° burned at the same mixture. It is noted
 pressure (v) and volume (v). The equation for the thermodynamic
 by which this relation is obtained is the same as the same mixture.
 3000° mixture, and that, from the same mixture, the mixture is
 3000° mixture, and that, from the same mixture, the mixture is

$$1 - \lambda^{\frac{1}{2}} \left(\frac{T}{T_0} \right)^{\frac{1}{2}} \quad \text{and} \quad 1 - \lambda^{\frac{1}{2}} \left(\frac{T}{T_0} \right)^{\frac{1}{2}} = \lambda^{\frac{1}{2}}$$

where $\lambda^{\frac{1}{2}}$ and $\lambda^{\frac{1}{2}}$ are the same as in the 1000° mixture, and
 it is the same as in the 1000° mixture. The mixture is the same
 value of the mixture is the same as in the 1000° mixture. The mixture
 3000° mixture, and that, from the same mixture, the mixture is
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 extrapolation. The mixture is the same as in the 1000° mixture. The mixture
 between the two mixtures, and the mixture is the same as in the
 limiting temperature are given, is the same as in the 1000° mixture and

Equation (4).

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APPENDIX I

L. 12.10.1912

TABLE I

Equilibrium Constants For Chemical Reactions

| T°R. | K ₁ | K ₂ | K ₃ | K ₄ | K ₅ | K ₆ |
|------|----------------|-------------------------|-------------------------|-------------------------|------------------------|------------------------|
| 3000 | 3.406 | 9.1658×10^{-8} | 1.816×10^{-10} | 3.981×10^{-10} | 1.014×10^{-4} | 5.053×10^{-6} |
| 3600 | 4.782 | 5.777×10^{-7} | 7.925×10^{-8} | 2.037×10^{-7} | 1.597×10^{-5} | 1.627×10^{-4} |
| 4500 | 6.455 | 3.512×10^{-4} | 3.451×10^{-5} | 9.122×10^{-5} | 2.514×10^{-2} | 5.232×10^{-3} |

$$K_1 = \frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}}$$

$$K_4 = \frac{P_O P_{H_2}}{P_{H_2O}}$$

$$K_2 = \frac{P_{NO} P_{H_2}}{P_{H_2O} P_{N_2}^{1/2}}$$

$$K_5 = \frac{P_H}{P_{H_2}^{1/2}}$$

$$K_3 = \frac{P_{O_2} P_{H_2}^2}{P_{H_2O}^2}$$

$$K_6 = \frac{P_{OH} P_{H_2}^{1/2}}{P_{H_2O}}$$

P_i in above is partial pressure in atmospheres, of each molecular species.

Equilibrium constants listed above were calculated from the series of values listed in Table 7, Appendix A, of Hotzel, Williams, and Satterfield (2) by interpolation, employing the linear relationship between the reciprocal of absolute temperature ($1/T^{\circ}K.$) and the natural logarithmic value of the equilibrium constant ($\log_e K_n$).

and the fact that the system is not yet fully operational.

2

[illegible]

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

11
10
9

1950

$\begin{array}{c} 0 \\ 1 \\ 1 \end{array} \bigg| \begin{array}{c} 1 \\ 1 \\ 0 \end{array}$
 $\begin{array}{c} 1 \\ 0 \\ 0 \end{array} \bigg| \begin{array}{c} 1 \\ 0 \\ 0 \end{array}$
 $\begin{array}{c} 1 \\ 0 \\ 0 \end{array}$

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|

[illegible]

5.

TABLE II

Thermodynamic Properties of Molecular Species

| Species | Internal Energy E | | | | Enthalpy H | | | |
|--------------------------------|----------------------|-------|-------|-------|---------------|-------|-------|-------|
| | 3000° | 3600° | 4500° | 5000° | 3600° | 4500° | 5000° | 5500° |
| CO ₂ | 14326 | 16448 | 24898 | 17638 | 22422 | 29866 | 34895 | 40317 |
| H ₂ O | 10659 | 13979 | 19301 | 13971 | 17953 | 24259 | 28251 | 32251 |
| Al ₂ H ₆ | 7765 | 9992 | 13266 | 11077 | 13966 | 18234 | 21234 | 24234 |
| O ₂ | 8396 | 10712 | 14301 | 11709 | 14686 | 19269 | 22269 | 25269 |
| CO | 75265 | 77467 | 80946 | 78577 | 81441 | 85814 | 88814 | 92814 |
| H ₂ | 64713 | 66733 | 69925 | 68030 | 70707 | 74895 | 77895 | 81895 |
| H | 84601 | 85594 | 87015 | 87913 | 89568 | 92053 | 94548 | 97043 |
| OH | 45423 | 47473 | 50721 | 48733 | 51447 | 55689 | 58689 | 62689 |
| NO | 29693 | 31928 | 36349 | 33003 | 35903 | 40317 | 43317 | 47317 |
| O | 62799 | 63792 | 65283 | 66111 | 67766 | 70251 | 72751 | 75251 |

The units of the above are calories /g-mole.

The values shown above were obtained from those in Table 6, Appendix A, Hottel, Williams, and Satterfield (2), in the following manner, using the internal energy of

species at as an example.

100

10. *How much time do you spend on the computer?*

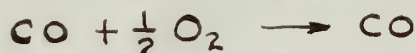
[illegible]

2. Let \mathcal{A} and \mathcal{B} be two algebras of sets. Then $\mathcal{A} \cup \mathcal{B}$ is an algebra of sets if and only if $\mathcal{A} \cap \mathcal{B}$ is an algebra of sets.

[illegible]

The internal energy of any species at temperature T equals $E_s + Q_v$ where E_s is the heat released by cooling the gas at constant volume to the temperature base of the chart ($100^\circ\text{F} = 311^\circ\text{K}$), and Q_v is the heat of combustion of the gas at constant volume at 100°F . E_s is the value of E of the species at temperature T minus the value of E of the species at 100°F , each obtained from Table 6, Appendix A, Hottel, Williams, and Satterfield (2). Q_v at 100°F is the heat evolved in cooling the species, and oxygen required for combustion, down to 0°K , plus the heat of combustion at 0°K (E at 0°K in Table 6), less the heat absorbed in heating the combustion products from 0°K to 311°K (100°F).

For the combustion of CO, the combustion equation is:



or one mole of specie CO reacts with one half mole of oxygen to form one mole of CO_2 as combustion products. From Table 6, Appendix A, Hottel, Williams, and Satterfield (2), the following values were obtained:

$$\text{For CO: } E_{0^\circ\text{K}} = 66,769$$

$$\text{For CO}_2: E_{311^\circ\text{K}} - E_{0^\circ\text{K}} = 1737$$

$$E_{311^\circ\text{K}} = 73,757$$

$$\text{For O}_2: E_{311^\circ\text{K}} - E_{0^\circ\text{K}} = 1538$$

$$E_{3600^\circ\text{R}} = 78,435$$

Then:

$$E_s = E_{3600^\circ\text{R}} - E_{311^\circ\text{K}} = 78435 - 73757 = 4678$$

$$\begin{aligned} Q_v &= [E_{311^\circ\text{K}} - E_{0^\circ\text{K}}]_{\text{CO}} + [E_{311^\circ\text{K}} - E_{0^\circ\text{K}}]_{\text{O}_2} \times \frac{1}{2} + [E_{0^\circ\text{K}}]_{\text{CO}_2} \\ &\quad - [E_{311^\circ\text{K}} - E_{0^\circ\text{K}}]_{\text{CO}_2} \\ Q_v &= (73757 - 66769) + \frac{1538}{2} + 66769 - 1737 \\ &= 72789 \end{aligned}$$

$$E_{3600^\circ\text{R}} = E_s + Q_v$$

$$= 4678 + 72789 = 77467 \text{ calories/g-mole.}$$

The above is the value shown in Table 2.

The latent energy of the system is given by $E_2 + Q_1$

where E_2 is the heat released in cooling the gas at constant volume

to the temperature T_2 of the gas (100°K) and Q_1 is the

heat of condensation of the gas at constant volume at 100°K. E_2 is the

value of E of the gas at the temperature T_2 minus the value of E of

the gas at 100°K, and Q_1 is the heat of condensation of the gas at 100°K.

Thus, the latent energy of the system is given by $E_2 + Q_1$ and the

latent energy of the system is given by $E_2 + Q_1$ and the

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$$CO + \frac{1}{2} O_2 \rightarrow CO$$

the heat of formation of CO is 110,517 J/mol at 298.15 K

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$$CO + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H_f^\circ = -110,517 \text{ J/mol}$$

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and the heat of formation of CO is 110,517 J/mol at 298.15 K

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$$CO + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H_f^\circ = -110,517 \text{ J/mol}$$

The heat of formation of CO is 110,517 J/mol at 298.15 K

The value of enthalpy is readily obtained from the relation $H = E + RT$.
Thus the enthalpy of CO at $T = 3600^{\circ}\text{R}$ is:

$$\begin{aligned} H_{3600^{\circ}\text{R}} &= E_{3600^{\circ}\text{R}} + 1.987 \times 2000 \\ &= 77467 + 3974 = 81441 \text{ calories/g-mole} \end{aligned}$$

TABLE III

Molar Entropy (at one atmosphere pressure)

| Species | 3000 ^o | 3600 ^o | 4500 ^o |
|--------------------|-------------------|-------------------|-------------------|
| CO ₂ | 20.166 | 22.522 | 25.791 |
| H ₂ O | 15.919 | 17.875 | 20.68 |
| Air-N ₂ | 12.754 | 14.143 | 16.072 |
| O ₂ | 13.490 | 14.956 | 16.993 |
| CO | 12.924 | 14.536 | 16.279 |
| H ₂ | 12.061 | 13.537 | 15.597 |
| H | 8.34 | 9.26 | 10.36 |
| OH | 12.40 | 13.74 | 15.62 |
| NO | 13.21 | 14.65 | 16.61 |
| O | 8.34 | 9.26 | 10.38 |

The units of the above are calories/g-mole $^{\circ}\text{K}$, or BTU/lb mole $^{\circ}\text{R}$.

The values shown in the above table (Table III) were obtained from those in Table 6, Appendix A, Hottel, Williams, and Satterfield (2), merely by subtracting the entropy value at the temperature base of the chart (100 $^{\circ}\text{F}$ 311 $^{\circ}\text{K}$) from the entropy corresponding to the temperature in question.

The value of α is calculated from the relation $\alpha = 180^\circ - \beta - \gamma$.

The value of β is calculated from the relation $\beta = 180^\circ - \alpha - \gamma$.

$$173000 \times 10^3 + 173000 \times 10^3 = 346000 \times 10^3$$

$$= 346000 + 346000 = 692000$$

TABLE III

Water content (%) and density (g/cm³)

| Water content (%) | Density (g/cm ³) | Water content (%) | Density (g/cm ³) |
|-------------------|------------------------------|-------------------|------------------------------|
| 0.00 | 1.000 | 0.00 | 1.000 |
| 0.10 | 0.999 | 0.10 | 0.999 |
| 0.20 | 0.998 | 0.20 | 0.998 |
| 0.30 | 0.997 | 0.30 | 0.997 |
| 0.40 | 0.996 | 0.40 | 0.996 |
| 0.50 | 0.995 | 0.50 | 0.995 |
| 0.60 | 0.994 | 0.60 | 0.994 |
| 0.70 | 0.993 | 0.70 | 0.993 |
| 0.80 | 0.992 | 0.80 | 0.992 |
| 0.90 | 0.991 | 0.90 | 0.991 |
| 1.00 | 0.990 | 1.00 | 0.990 |

The value of α is calculated from the relation $\alpha = 180^\circ - \beta - \gamma$.

The value of β is calculated from the relation $\beta = 180^\circ - \alpha - \gamma$.

where α is the angle between the two sides of the triangle, β is the angle between the two sides of the triangle, and γ is the angle between the two sides of the triangle. The value of α is calculated from the relation $\alpha = 180^\circ - \beta - \gamma$.

TABLE IV

Thermodynamic Properties of Equilibrium Mixture of Combustion Products
From Which Charts Were Constructed;

150% AIR

| T | P | E | H | S | V |
|--------------------|------|---------|----------|--------|--------|
| $^{\circ}\text{R}$ | psi | BTU | BTU | BTU/ | cu.ft. |
| 3000 | 800 | 546.556 | 752.499 | .26154 | 1.4647 |
| 3000 | 1200 | 546.546 | 752.478 | .23382 | .9764 |
| 3000 | 1500 | 546.535 | 752.467 | .21402 | .7812 |
| 3600 | 800 | 711.280 | 959.210 | .31630 | 1.7579 |
| 3600 | 1000 | 711.174 | 959.102 | .30150 | 1.4963 |
| 3600 | 1200 | 711.091 | 959.021 | .28899 | 1.1719 |
| 3600 | 1400 | 711.025 | 958.956 | .27842 | 1.0045 |
| 3600 | 1500 | 710.997 | 958.928 | .27343 | .9375 |
| 4500 | 800 | 972.820 | 1281.711 | .39186 | 2.2028 |
| 4500 | 1200 | 970.082 | 1278.913 | .36448 | 1.4678 |
| 4500 | 1500 | 968.667 | 1277.560 | .34939 | 1.1741 |

250% AIR

| T | P | E | H | S | V |
|--------------------|------|---------|----------|--------|--------|
| $^{\circ}\text{R}$ | psu | BTU | BTU | BTU/ | cu.ft. |
| 3000 | 800 | 522.589 | 728.525 | .24278 | 1.4287 |
| 3000 | 1200 | 522.578 | 728.513 | .21533 | .9524 |
| 3000 | 1500 | 522.570 | 728.508 | .20005 | .7620 |
| 3600 | 800 | 682.240 | 930.719 | .24695 | 1.7115 |
| 3600 | 1000 | 682.166 | 930.645 | .28166 | 1.3718 |
| 3600 | 1200 | 682.098 | 930.577 | .26915 | 1.1431 |
| 3600 | 1400 | 682.056 | 930.537 | .25859 | .9798 |
| 3600 | 1500 | 682.029 | 930.509 | .25389 | .9145 |
| 4500 | 800 | 927.830 | 1236.720 | .36928 | 2.1468 |
| 4500 | 1200 | 925.784 | 1235.127 | .34204 | 1.4308 |
| 4500 | 1500 | 925.440 | 1234.331 | .32676 | 1.1445 |

The material basis consistent with the above values is one pound of dry air ($1/28.95$ pound-mole), plus the corresponding fuel.

Table 2000

| Year | Age | Sex | Height | Weight | Stature | Age |
|------|-----|-----|--------|--------|---------|-----|
| 1900 | 10 | M | 150 | 100 | 150 | 10 |
| 1901 | 11 | M | 155 | 105 | 155 | 11 |
| 1902 | 12 | M | 160 | 110 | 160 | 12 |
| 1903 | 13 | M | 165 | 115 | 165 | 13 |
| 1904 | 14 | M | 170 | 120 | 170 | 14 |
| 1905 | 15 | M | 175 | 125 | 175 | 15 |
| 1906 | 16 | M | 180 | 130 | 180 | 16 |
| 1907 | 17 | M | 185 | 135 | 185 | 17 |
| 1908 | 18 | M | 190 | 140 | 190 | 18 |
| 1909 | 19 | M | 195 | 145 | 195 | 19 |
| 1910 | 20 | M | 200 | 150 | 200 | 20 |
| 1911 | 21 | M | 205 | 155 | 205 | 21 |
| 1912 | 22 | M | 210 | 160 | 210 | 22 |
| 1913 | 23 | M | 215 | 165 | 215 | 23 |
| 1914 | 24 | M | 220 | 170 | 220 | 24 |
| 1915 | 25 | M | 225 | 175 | 225 | 25 |
| 1916 | 26 | M | 230 | 180 | 230 | 26 |
| 1917 | 27 | M | 235 | 185 | 235 | 27 |
| 1918 | 28 | M | 240 | 190 | 240 | 28 |
| 1919 | 29 | M | 245 | 195 | 245 | 29 |
| 1920 | 30 | M | 250 | 200 | 250 | 30 |

The recorded data are given in the following table.

of the air (1/1000) and the pressure (1/1000).

APPENDIX II

II. SUMMARY

Method of Calculating Composition of Combustion Products In Equilibrium

The large number of molecular species present in the combustion equilibrium mixture makes it necessary to organize the method of calculation to minimize trial-and-error.

There are four kinds of atoms present (C, H, O, N). These are distributed in ten species (CO_2 , H_2O , O_2 , N_2 , CO , H_2 , H , OH , NO , O). Available in relating these species are the six chemical equilibrium equations shown in Table I, Appendix I. They are listed again here for convenient reference, with the number of moles of each species being represented by its chemical symbol in parenthesis:

$$\text{Eq. 1} \quad K_1 = P_{\text{CO}} P_{\text{H}_2\text{O}} / P_{\text{CO}_2} P_{\text{H}_2} = (\text{CO})(\text{H}_2\text{O}) / (\text{CO}_2)(\text{H}_2)$$

$$\text{Eq. 2} \quad K_2 = P_{\text{NO}} P_{\text{H}_2} / P_{\text{H}_2\text{O}} P_{\text{N}_2}^{1/2} = (\text{NO})(\text{H}_2) / (\text{H}_2\text{O})(\text{N}_2)^{1/2} \times \sqrt{P/\sum}$$

$$\text{Eq. 3} \quad K_3 = P_{\text{O}_2} P_{\text{H}_2}^2 / P_{\text{H}_2\text{O}}^2 = (\text{O}_2)(\text{H}_2)^2 / (\text{H}_2\text{O})^2 \times \frac{P}{\sum}$$

$$\text{Eq. 4} \quad K_4 = P_{\text{O}} P_{\text{H}_2} / P_{\text{H}_2\text{O}} = (\text{O})(\text{H}_2) / (\text{H}_2\text{O}) \times \frac{P}{\sum}$$

$$\text{Eq. 5} \quad K_5 = P_{\text{H}} / P_{\text{H}_2}^{1/2} = (\text{H}) / (\text{H}_2)^{1/2} \times \sqrt{P/\sum}$$

$$\text{Eq. 6} \quad K_6 = P_{\text{OH}} P_{\text{H}_2}^{1/2} / P_{\text{H}_2\text{O}} = (\text{OH})(\text{H}_2)^{1/2} / (\text{H}_2\text{O}) \times \sqrt{P/\sum}$$

In the above, P is the total pressure in atmospheres, P_i is the partial pressure in atmospheres of each molecular species, and the symbol \sum represents the sum of the moles of all species present.

As shown in Chapter III (4), with a fuel-air ratio of 0.77, or 130% air, there are 1.95 moles of O_2 and 7.332 moles of N_2 present, giving 9.282 moles of air per mole of fuel; with a fuel-air ratio of) .4, or 250% air, there are 3.75 moles of O_2 and 14.1 moles of N_2 present, giving 17.85 moles of air per mole of fuel. If one mole of carbon and of hydrogen in the fuel is chosen as a basis, there are available the following

The first moment of molecular species present in the medium

is defined as follows: it is necessary to assume the mass of

molecules in equilibrium with the medium.

There are two kinds of mass moments (M_1, M_2, \dots, M_n). These are

distributed in the species $H_2, O, H_2O, CO, CO_2, H_2O_2, \dots$

which is defined as follows: these species are in chemical equilibrium

equations given in Table 1, Appendix 1. The first three are for

chemical reactions, and the fourth of mass of each species being

represented by the species $H_2, O, H_2O, CO, CO_2, H_2O_2, \dots$

$$Ed.1 \quad K_1 = \frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}} = \frac{(CO)(H_2O)}{(CO_2)(H_2)}$$

$$Ed.2 \quad K_2 = \frac{P_{H_2O}}{P_{H_2} P_{O_2}} = \frac{(H_2O)}{(H_2)(O)}$$

$$Ed.3 \quad K_3 = \frac{P_{CO_2}}{P_{CO} P_{O_2}} = \frac{(CO_2)}{(CO)(O)}$$

$$Ed.4 \quad K_4 = \frac{P_{H_2O_2}}{P_{H_2} P_{O_2}} = \frac{(H_2O_2)}{(H_2)(O)}$$

$$Ed.5 \quad K_5 = \frac{P_{H_2O}}{P_{H_2} P_{O_2}} = \frac{(H_2O)}{(H_2)(O)}$$

$$Ed.6 \quad K_6 = \frac{P_{CO_2}}{P_{CO} P_{O_2}} = \frac{(CO_2)}{(CO)(O)}$$

In the above, P is the total pressure in equilibrium, P_i is the

partial pressure of species i in equilibrium with the other

species. \sum represents the sum of the mass of all species present.

At equilibrium (Table 1), with a constant mass of 1.0 g, the

air, water and 1.0 g of H_2 and 1.0 g of O_2 present, giving

1.0 g of air, water and 1.0 g of H_2 and 1.0 g of O_2 present, giving

air, water and 1.0 g of H_2 and 1.0 g of O_2 present, giving

1.0 g of air, water and 1.0 g of H_2 and 1.0 g of O_2 present, giving

and in the case of 1.0 g of H_2 and 1.0 g of O_2 present, giving

four equations satisfying the material balance of the four atoms present (C, H, O, N). These equations are, on a mole basis, at equilibrium:

$$\text{Eq. 7} \quad (\text{CO}_2) + (\text{CO}) = 1.000$$

$$\text{Eq. 8} \quad (\text{H}_2\text{O}) + (\text{H}_2) + \frac{1}{2}[(\text{H}) + (\text{OH})] = 1.000$$

$$\text{Eq. 9} \quad (\text{CO}_2) + (\text{O}_2) + \frac{1}{2}[(\text{H}_2\text{O}) + (\text{CO}) + (\text{OH}) + (\text{NO}) + (\text{O})] = 3.75$$

$$\text{Eq. 10} \quad (\text{N}_2) + \frac{1}{2}(\text{NO}) = 14.1$$

The equations 1 to 10 inclusive give sufficient relations to solve for the composition of the ten molecular species in the combustion products.

Procedure: The first step is to divide the ten species into major components (CO_2 , H_2O , O_2 , N_2 , CO and H_2), and minor components (H_2O , NO , and OH) and to consider for the first approximation of composition that only major components are present. Then equations 7 to 10 inclusive

become: $\text{Eq. 7A} \quad (\text{CO}_2) + (\text{CO}) = 1.000$

$$\text{Eq. 8A} \quad (\text{H}_2\text{O}) + (\text{H}_2) = 1.000$$

$$\text{Eq. 9A} \quad (\text{CO}_2) + (\text{O}_2) + \frac{1}{2}[(\text{H}_2\text{O}) + (\text{CO})] = 3.75$$

$$\text{Eq. 10A} \quad (\text{N}_2) = 14.1$$

$$\text{Eq. 11} \quad \Sigma = (\text{CO}_2) + (\text{H}_2\text{O}) + (\text{O}_2) + (\text{N}_2) + (\text{CO}_2) + (\text{H}_2)$$

By judicious use of the above five equations together with equations 1 and 3, a first approximation of the number of moles of the major species present may be obtained. Then, using these results, plus equations 2, 4, 5 and 6, a first approximation of the minor species is made. The values of the minor species so obtained are put onto the original four equations 7, 8, 9, and 10 and these equations in turn solved in terms of the major species. A second approximation is now

These equations, together with material balances on the total system, provide (7, 8, 9, 10) four equations for the four species, H_2 , CO , CO_2 , and H_2O .

$$\begin{aligned} \text{Eq. 7} \quad & (CO_2) + (CO) = 1.000 \\ \text{Eq. 8} \quad & (H_2O) + (H_2) + \frac{1}{2}[(H) + (OH)] = 1.000 \\ \text{Eq. 9} \quad & (CO_2) + (CO) + \frac{1}{2}[(H_2O) + (H_2) + (OH) + (H)] = 3.72 \\ \text{Eq. 10} \quad & (H_2) + \frac{1}{2}(H) = 14.1 \end{aligned}$$

The equations 7 to 10 involve four unknown species to solve for the composition of the gas mixture. In the equations, the species are:

Species: H_2 , CO , CO_2 , and H_2O . The total number of species is four. The total number of atoms is 14.1 for H and 3.72 for C . The total number of molecules is 1.000.

$$\begin{aligned} \text{Eq. 7A} \quad & (CO_2) + (CO) = 1.000 \\ \text{Eq. 8A} \quad & (H_2O) + (H_2) = 1.000 \\ \text{Eq. 9A} \quad & (CO_2) + (CO) + \frac{1}{2}[(H_2O) + (H_2) + (OH) + (H)] = 3.72 \\ \text{Eq. 10A} \quad & (H_2) = 14.1 \\ \text{Eq. 11} \quad & \sum = (CO_2) + (H_2O) + (CO) + (H_2) + (H) + (OH) \end{aligned}$$

If balance is maintained, the equations are solved. The total number of species is four. The total number of atoms is 14.1 for H and 3.72 for C . The total number of molecules is 1.000. The species are: H_2 , CO , CO_2 , and H_2O .

carried out, in precisely the same manner as the first approximation, to give corrected values of the major species based upon the presence of minor species. Again values of the minor species are determined with the aid of equations 2, 4, 5 and 6. If the results for all species satisfy equations 7, 8, 9, and 10, the computation is completed; if not, further approximations are carried through until these equations are perfectly satisfied.

To illustrate the method, a sample calculation will be carried out, using representative values of temperature and pressure.

$$T = 3000^{\circ} \quad p = 1200 \text{ psi} \quad P = 81.65 \text{ atmospheres} \quad 250\% \text{ air}$$

From Table I, Appendix I, at $T = 3000^{\circ} \text{ R.}$

$$K_1 = 3.406$$

$$K_4 = 3.981 \times 10^{-10}$$

$$K_2 = 9265 \times 10^{-8}$$

$$K_5 = 1.014 \times 10^{-4}$$

$$K_3 = 1.816 \times 10^{-10}$$

$$K_6 = 5.053 \times 10^{-6}$$

$$\text{Eq. 1. } \frac{(CO)(H_2O)}{(CO_2)(H_2)} = K_1 = 3.406$$

$$\text{Eq. 3. } \frac{(O_2)(H_2)^2}{(H_2O)^2} = K_3 \left[\frac{\Sigma}{P} \right] = 1.816 \times 10^{-10} \left[\frac{\Sigma}{P} \right]$$

or

$$\frac{(H_2)}{(H_2O)} = 1.347 \times 10^{-5} \left[\sqrt{\frac{\Sigma}{P(O_2)}} \right]$$

Adding equations 7A, 8A, and 10A:

$$\text{Eq. 12 } (CO_2) + (CO) + (H_2O) + (H_2) + (N_2) = 16.1$$

$$\text{Eq. 13 } \Sigma = 16.1 + (O_2)$$

Multiplying equation 9A by two and subtracting equation 7A:

$$\text{Eq. 14. } (CO_2) + (H_2O) + 2(O_2) = 6.5$$

carried out, it is possible to have a number of different types of reactions. The first type is a simple reaction, in which the reactants are combined to form a single product. The second type is a complex reaction, in which the reactants are combined to form a series of intermediate products, which are then combined to form the final product. The third type is a reversible reaction, in which the reactants are combined to form a product, which can then react with other substances to form the reactants again. The fourth type is a catalyzed reaction, in which the reactants are combined to form a product, but the reaction is accelerated by the presence of a catalyst. The fifth type is a reaction that is affected by temperature, pressure, or concentration. In all of these cases, the reaction is carried out under conditions that are as close as possible to the ideal conditions for the reaction.

For illustration the reaction of hydrogen and oxygen is used. The reaction is carried out at a pressure of 1 atm and a temperature of 25°C. The reaction is carried out in a closed system, and the reactants are mixed in a 2:1 ratio by volume. The reaction is carried out for a period of 10 minutes, and the products are then analyzed.

$T = 298.15 \text{ K}$ $P = 1.01325 \times 10^5 \text{ Pa}$ $P = 1.01325 \text{ bar}$ $T = 298.15 \text{ K}$

$$K_1 = 1.0 \times 10^{-10} \quad K_2 = 1.0 \times 10^{-10} \quad K_3 = 1.0 \times 10^{-10} \quad K_4 = 1.0 \times 10^{-10} \quad K_5 = 1.0 \times 10^{-10}$$

$$Ed. 1 \quad \frac{(CO)(H_2O)}{(CO_2)(H_2)} = K_1 = 3.46$$

$$Ed. 2 \quad \frac{(O_2)(H_2)}{(H_2O)^2} = K_2 = 1.81 \times 10^{-10} \left[\frac{2}{9} \right]$$

$$OR \quad \frac{(H_2O)}{(H_2)} = 1.341 \times 10^{-2} \left[\sqrt{\frac{2}{9(O_2)}} \right]$$

$$Ed. 12 \quad (CO) + (CO) + (H_2O) + (H_2) + (H_2) = 16.1$$

$$Ed. 13 \quad 2 = 16.1 + (O_2)$$

$$Ed. 14 \quad (CO_2) + (H_2O) + 2(O_2) = 6.2$$

From equation 10A

$$(N_2) = 14.1$$

1ST APPROXIMATION

| | | 1. | 2. |
|--|----------|-------------------------|------------------------|
| (O_2) | | 2.25009 | 2.2500094 |
| $\Sigma = 16.1 + (O_2)$ | [Eq. 13] | 18.35009 | 18.3500094 |
| $\sqrt{\frac{\Sigma}{P(O_2)}}$ | | .316035 | .316035 |
| $\frac{(H_2)}{(H_2O)} = 1.347 \times 10^{-5} \sqrt{\frac{\Sigma}{P(O_2)}}$ | [Eq. 3] | $.42569 \times 10^{-5}$ | $.4257 \times 10^{-5}$ |
| (H_2) | | .0000042569 | .000004257 |
| $(H_2O) = 1.000 - (H_2)$ | [Eq. 8A] | .9999957431 | .999995743 |
| $(CO_2) = 6.5 - 2(O_2) - (H_2O)$ | [Eq. 14] | — | .999985457 |
| $(CO) = 1.000 - (CO_2)$ | [Eq. 7A] | — | .000014543 |
| $\frac{(CO)(H_2O)}{(CO_2)(H_2)} = 3.406$ | [Eq. 1] | — | 3.410 |

$$\begin{aligned} \text{Eq. 5} \quad (H) &= (K_5) \cdot (H_2)^{1/2} \cdot \sqrt{\frac{\Sigma}{P}} \\ &= 1.014 \times 10^{-4} \times .000004257^{1/2} \times \sqrt{\frac{18.3500094}{81.65}} \\ &= .0000000992 \end{aligned}$$

$$\begin{aligned} \text{Eq. 6} \quad (OH) &= (K_6) \cdot \frac{(H_2O)}{(H_2)^{1/2}} \cdot \sqrt{\frac{\Sigma}{P}} \\ &= (5.053 \times 10^{-6}) \cdot \frac{(.999995743)}{(.000004257)^{1/2}} \cdot \sqrt{\frac{18.3500094}{81.65}} \\ &= .00116094 \end{aligned}$$

$$I(A) = (2N)$$

5. 520000 5. 520000

4200025.81 00025.81 [E-13]

28021E. 28021E

4520×10^{-2} 4520×10^{-2} 4520×10^{-2}

725400000. 8025400000.

3472 P0000. 15472 P0000. [A8 P3]

74280000.

842410000. [A7.95]

014.C

$$= 1.04 \times 10^{-4} \times 0.000452 \times \sqrt{15.20034} \times 8.92$$

see oooooooooo

$$E_d = \frac{(OH)^2}{(K_2)^{1/2} \cdot (H_2O)} \cdot \sqrt{\frac{D}{t}}$$

$$\frac{4800025.81}{20.18} \sqrt{\frac{(847299999.)}{(725400000.)}} (2.01 \times 520.2) =$$

49021100. =

$$\begin{aligned}
 \text{Eq. 2} \quad (NO) &= K_2 \cdot \frac{(H_2O)}{(H_2)} \cdot (N_2)^{1/2} \cdot \sqrt{\frac{Z}{P}} \\
 &= (9.165 \times 10^{-8}) \cdot \frac{.999995743}{.000004257} \cdot 14.1^{1/2} \cdot \sqrt{\frac{18.3500094}{81.65}} \\
 &= .0383043
 \end{aligned}$$

$$\begin{aligned}
 \text{Eq. 4} \quad (O) &= K_4 \cdot \frac{(H_2O)}{(H_2)} \cdot \frac{Z}{P} \\
 &= (3.981 \times 10^{-10}) \cdot \frac{.999995743}{.000004257} \cdot \frac{18.3500094}{81.65} \\
 &= .000021015
 \end{aligned}$$

Substituting these values for the minor species in equations

7, 8, 9 and 10:

$$\text{Eq. 7} \quad (CO_2) + (CO) = 1.000$$

$$\begin{aligned}
 \text{Eq. 8} \quad (H_2O) + (H_2) &= 1.000 - \frac{1}{2} [(H) + (OH)] \\
 &= .99941948
 \end{aligned}$$

$$\begin{aligned}
 \text{Eq. 9} \quad (CO_2) + (O_2) + \frac{1}{2} [(H_2O) + (CO)] &= 3.750 - \frac{1}{2} [(OH) + (NO) + (O)] \\
 &= 3.730247
 \end{aligned}$$

$$\begin{aligned}
 \text{Eq. 10} \quad (N_2) &= 14.1 - \frac{1}{2} (NO) \\
 &= 14.080848
 \end{aligned}$$

Now, following the same procedure as before:

Adding Eq. 7, 8, and 10;

$$\text{Eq. 12A} \quad (\text{CO}_2) + (\text{CO}) + (\text{H}_2\text{O}) + (\text{H}_2) + (\text{N}_2) = 16.0802675$$

$$\text{Eq. 13A} \quad \Sigma = 16.0802675 + (\text{O}_2)$$

Multiplying Eq. 9 by two and subtracting Eq. 7:

$$\text{Eq. 14A} \quad (\text{CO}_2) + (\text{H}_2\text{O}) + 2(\text{O}_2) = 6.460494$$

2ND APPROXIMATION

| | 1. | 2. |
|--|-------------------------|-------------------------|
| (O_2) | 2.23055 | 2.2305437 |
| $\Sigma = 16.080257 + (\text{O}_2)$ | 18.310807 | 18.3108007 |
| $\sqrt{\frac{\Sigma}{P(\text{O}_2)}}$ | .317071 | .317071 |
| $\frac{(\text{H}_2)}{(\text{H}_2\text{O})} = 1.347 \times 10^{-5} \sqrt{\frac{\Sigma}{P(\text{O}_2)}}$ | .42709 $\times 10^{-5}$ | .42709 $\times 10^{-5}$ |
| (H_2) | .00000427 | .00000427 |
| $(\text{H}_2\text{O}) = 0.99941947 - (\text{H}_2)$ | .99941520 | .9994152 |
| $(\text{CO}_2) = 6.460492 - 2(\text{O}_2) - (\text{H}_2\text{O})$ | — | .99998545 |
| $(\text{CO}) = 1.000 - \text{CO}_2$ | — | .00001455 |
| $\frac{(\text{CO})(\text{H}_2\text{O})}{(\text{CO}_2)(\text{H}_2)} = 3.406$ | | 3.405 |

Again determining the minor species from Eqs. 5, 6, 2 and 4:

$$\begin{aligned} (\text{H}) &= .0000000992 \\ (\text{OH}) &= .00115729 \\ (\text{NO}) &= .038121 \\ (\text{O}) &= .000020895 \end{aligned}$$

$$E.d.13A \quad (CO_2) + (CO) + (H_2O) + (H_2) + (H_2) = 12.080.21$$

$$E.d.13A \quad E = 12.080.21 + (O_2)$$

Not to be used for any other purpose

$$E.d.14A \quad (CO_2) + (H_2O) + (O_2) = 8.480.43$$

NOT RECOMMENDED

| | | |
|--------------------|--------------------|--|
| | | (O_2) |
| $18.310.000$ | $18.310.81$ | $E = 12.080.21 + (O_2)$ |
| $15.051.2$ | $15.051.2$ | $\sqrt{\frac{E}{b(O_2)}}$ |
| 2.51×10^6 | 2.51×10^6 | $\frac{E}{b(O_2)} = 1.94 \times 10^{-2}$ |
| $758.000.00$ | $758.000.00$ | (H_2) |
| 521.000 | 521.000 | $(H_2O) = 0.6841045 - (H_2)$ |
| $347.888.00$ | — | $(CO_2) = 0.480405 - 5(O_2) - (H_2O)$ |
| $34.000.00$ | — | $(CO) = 1.000 - CO_2$ |
| 3.402 | | $\frac{(CO)(H_2O)}{(CO_2)(H_2)} = 3.402$ |

Not to be used for any other purpose

- $(H) = 220.000.000$
- $(H_2) = 55.721.00$
- $(H_2O) = 0.32151$
- $(O) = 0.00050832$

The values of these species have not changed from those obtained in the first approximation, to any extent, and hence all values satisfy equations 7, 8, 9 and 10; if they had not, a third approximation would have been required, performed in the same manner as the above.

Final Results:

$$(CO_2) = .99998545$$

$$(H_2O) = .9994152$$

$$(O_2) = 2.2305437$$

$$(N_2) = 11.08094$$

$$(CO) = .00001455$$

$$(H_2) = .00000427$$

$$(H) = .0000000992$$

$$(OH) = .00115729$$

$$(NO) = .038121$$

$$(O) = .000020895$$

The value of the function $f(x)$ is given by the following table. The values of $f(x)$ are given for x from 0 to 10. The values of $f(x)$ are given for x from 0 to 10. The values of $f(x)$ are given for x from 0 to 10.

TABLE 1

| | | |
|----------|---|-----|
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |
| 0.000000 | = | (0) |

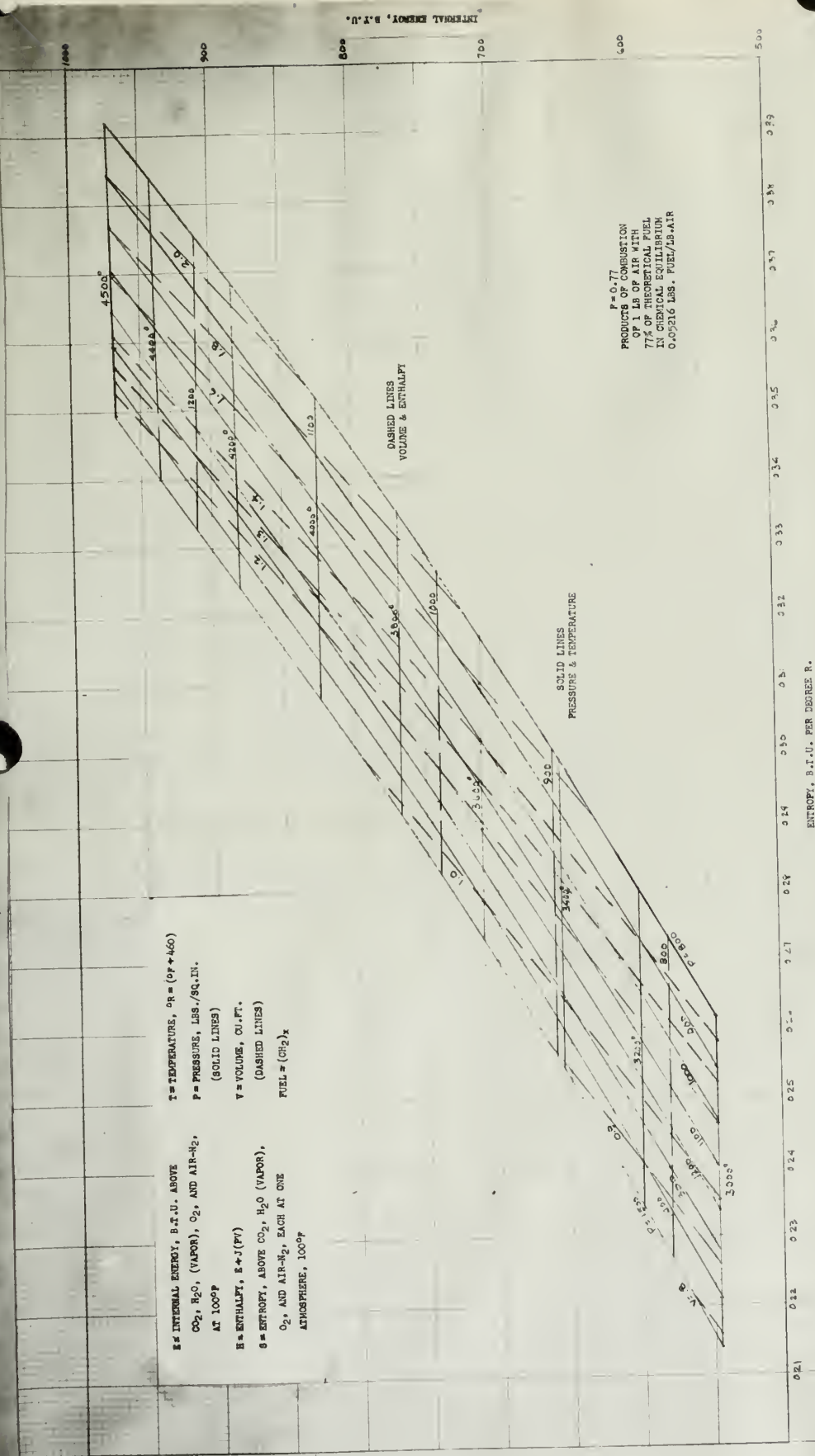
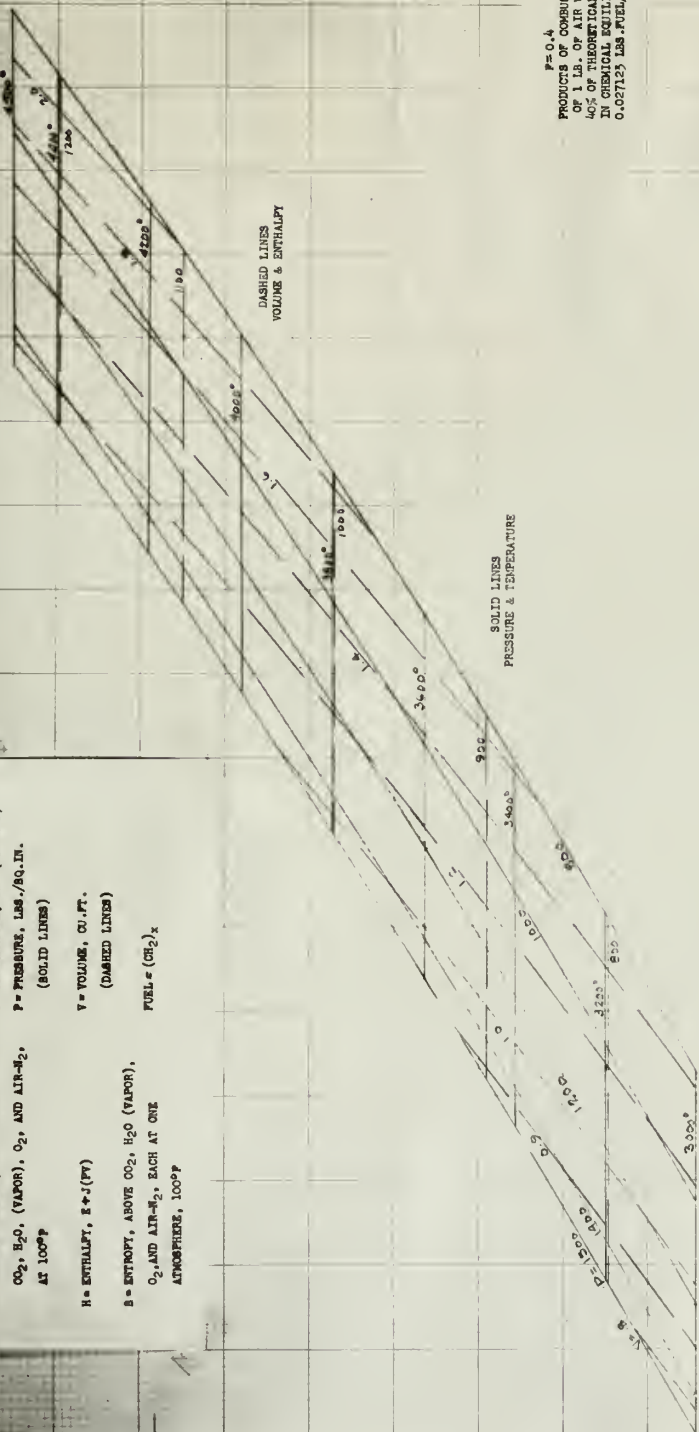


Fig I



E = INTERNAL ENERGY, B.T.U. ABOVE
 CO_2 , H_2O , (VAPOR), O_2 , AND AIR-H_2 ,
 AT 100°F
 H = ENTHALPY, $E + J(\text{FT})$
 S = ENTROPY, ABOVE CO_2 , H_2O (VAPOR),
 O_2 , AND AIR-H_2 , EACH AT ONE
 ATMOSPHERE, 100°F
 T = TEMPERATURE, $^\circ\text{R}$ (°F + 460)
 P = PRESSURE, LBS./SQ. IN.
 (SOLID LINES)
 V = VOLUME, CU. FT.
 (DASHED LINES)
 $\text{FUEL } e (\text{CH}_2)_x$



$P = 0.4$
 PRODUCTS OF COMBUSTION
 OF 1 LB. OF AIR WITH
 46% THEORETICAL FUEL
 IN CHEMICAL EQUILIBRIUM
 0.027123 LBS FUEL/LB AIR

Fig Ia



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the combustion process in
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